

REMARKS

The rejection of Claims 1-18 under 35 U.S.C. § 103(a) as unpatentable over US 5,107,038 (Weinstein) and US 3,177,258 (Rylander et al), and further in view of US 6,002,047 (Jansen et al), is respectfully traversed.

The present invention relates to a novel method of hydrogenating a phenol that enables an industrial important phenol hydrogenation process to be carried out as an environmentally friendly process that requires no harmful organic solvents, and more specifically relates, for example, to a method of efficiently hydrogenating a phenol using carbon dioxide, such as super critical carbon dioxide, and a highly active supported rhodium and/or ruthenium catalyst that can be carried out at a lower reaction temperature than compared to the prior art, while preventing a drop in activity of the catalyst.

As discussed in further detail below, the results obtained by combining the presence of carbon dioxide with a rhodium and/or ruthenium catalyst, are surprisingly superior to analogous combinations using other platinum group metals, such as platinum and palladium.

Weinstein is drawn to a process for preparation of 4-tert-butyl-cyclohexanol by hydrogenating 4-tert-butyl-phenol or 4-tert-butyl-cyclohexanone in the presence of a catalytic system comprising supported rhodium in combination with a particular boron-fluorine compound cocatalyst, the object of which is to produce the 4-tert-butyl-cyclohexanol essentially in the form of its cis isomer (paragraph bridging columns 2 and 3). The hydrogenation takes place in an organic solvent (paragraph bridging columns 3 and 4).

Rylander et al relates to the hydrogenation of certain organic compounds using a ruthenium-containing catalyst combined with another platinum group metal, such as platinum, palladium or rhodium (column 1, lines 10-15), which certain organic compounds are inclusive of a wide variety of compounds, including phenols (column 1, line 57ff). Of all the examples disclosed in Rylander et al, only Example 6 therein relates to the hydrogenation

of phenols. Table V therein displays the data for Example 6 using various platinum group metals on various phenol compounds in terms of hydrogen consumed. Applicants will further discuss this data later in this response.

Recognizing that neither Weinstein nor Rylander et al discloses conducting hydrogenation in the presence of carbon dioxide, the Examiner relies on Jansen et al. However, Jansen et al does not remedy the above-discussed deficiencies in Weinstein and Rylander et al.

Jansen et al is drawn to the catalytic hydrogenation of organic compounds on a catalyst of amorphous metal alloys under near-critical or super critical conditions of a solvent (column 1, lines 9-12), wherein the amorphous metal alloys are metallic glasses that are nonporous and may be contrasted with, for example, finely dispersed palladium catalysts carried on an active charcoal (column 1, lines 28-36), wherein super critical carbon dioxide is the preferred solvent (column 4, line 3ff). Jansen et al further discloses that their process can be used in all conventional hydrogenation reactions on organic compounds (column 4, lines 22-23). While Jansen et al lists ring hydrogenation of aromatic compounds (column 4, lines 28-29), there is no particular disclosure of hydrogenating phenols, nor are any of the examples therein drawn to hydrogenation of phenols.

In Jansen et al, the use of super critical carbon dioxide is with a particular catalyst, i.e., an amorphous metal alloy or metallic glass which, as discussed above, is distinguished by Jansen et al from supported platinum group metals (palladium) catalysts. It is impossible to predict, and there is no disclosure or suggestion in any of the applied prior art, what effect, good or bad or no, super critical carbon dioxide would have when used with such a platinum metal group-supported catalyst.

At best, the Examiner has made out an “obvious to try” rationale. “Obvious to try” has long been held not to constitute obviousness. *In re O’Farrell*, 853 F.2d 894, 7 USPQ2d

1673, 1680-81 (Fed. Cir. 1988) (**copy enclosed**). A general incentive does not make obvious a particular result, nor does the existence of techniques by which those efforts can be carried out. *In re Deuel*, 51 F.3d 1552, 34 USPQ2d 1210, 1216 (Fed. Cir. 1995) (**copy enclosed**).

In sum, the applied prior art does not make out a *prima facie* case of obviousness. Nevertheless, even if such a case were made out, the comparative data in the specification herein overcomes such a case. However, prior to discussing this data, Applicants now discuss Example 6 of Rylander et al, alluded to above. Example 6 of Rylander et al is the result of an investigation of the hydrogenation of phenols and alkoxy benzenes using seven catalysts in 50 ml of water.

As described in Example 6 of Rylander et al, 300mg of catalyst, 50ml of water and 0.1mol of substrate were charged to a Parr shaking apparatus, pressured to 50 p.s.i.g. with H₂. The shaker was started and the pressure drop recorded as a function of time. Consumed H₂ was calculated. On the equipment, 8 p.s.i.g. pressure charge is 0.1 mol of H₂ (column 8, lines 1-11). The four phenols used as a substrate are all soluble in water. Rylander et al merely analyzed the amount of consumed H₂, but did not investigate yield. Thus, there does not appear to be investigation of the extent of hydrogenation or not.

In each case, average hydrogenation rate over the initial four hour period is given in ml/min. and used to compare catalyst activity (column 7, line 42 - column 8, line 10). The results from said Table V of said Example 6 for the three catalysts, 5% Pt/C, 5% Ru/C and 5% Pd/C, on the hydrogenation of phenols such as a phenol, resorcinol, hydroquinone and p-methoxy phenol, in 50ml of water, are shown in an Abridged Table V below:

Abridged Table V
(Effect of catalysts, 5% Pt/C, 5% Ru/C and 5% Pd/C on the hydrogenation of phenol, resorcinol, hydroquinone and p-methoxy phenol, in water (50ml))

| Catalyst | | Substrate | | Measured H ₂ adsorption rate | | | ml/min. |
|----------|---------|-----------|-----|---|------------|--------------|-----------|
| No | Name | Amount | | Phenol | Resorcinol | Hydroquinone | p-Methoxy |
| | | Mg | mol | | | | phenol |
| 1 | 5% Pt/C | 300 | 0.1 | 4.6 | 4.0 | 3.0 | 6.2 |
| 2 | 5% Ru/C | 300 | 0.1 | 2.0 | 0 | 0 | 0 |
| 4 | 5% Pd/C | 300 | 0.1 | 1.5 | 0.6 | 0 | 0 |

The 5% Pt/C catalyst is active in the hydrogenation reaction for all four of the phenols, the 5% Pd/C catalyst is active for phenol and resorcinol only, and the 5% Ru/C catalyst is active only for phenol. This experimental results of Rylander et al indicate that the hydrogenation activities of platinum group metal catalysts such as 5% Pt/C, 5% Ru/C and 5% Pd/C vary from active to inactive, depending on the particular substrate phenol, even if under similar conditions of water fluid, temperature and pressure. Thus, for example, hydrogenation activity for a given phenol substrate using any of these catalysts is difficult, if not impossible, to predict.

The values of hydrogenation conversion ratio for phenol after 4 hrs are estimated in order to realize the degree of catalyst activities for 5% Pt/C, 5% Ru/C and 5% Pd/C. At first, the values of amount of hydrogen adsorption during the 4 hour hydrogenation reaction, are calculated from the rate data in Abridged Table V and reaction time, 4 hrs (240 minute). After that, the values of hydrogenation conversion ratio after 4 hrs are calculated from the amount of hydrogen adsorption after 4 hrs on the assumption that the yield selectivity of cyclohexanone/cyclohexanol is 50%/50%. In this case, 1 mol of phenol is hydrogenated by

2.5 mol of hydrogen. Estimated values of conversion ratio are indicated in modified Table V below:

Modified Table V
(Effect of three catalysts, 5% Pt/C, 5% Ru/C and 5% Pd/C on the hydrogenation of phenol in water (50ml))

| No | Name | Amount | H ₂ adsorption | | | **Estimated conversion ratio after 4 hrs |
|----|---------|--------|---------------------------|-----|----------------|--|
| | | | Phenol | | | |
| | | | mg | mol | Rate ml/min | |
| 1 | 5% Pt/C | 300 | 0.1 | 4.6 | 1104 | 17.9 |
| 2 | 5% Ru/C | 300 | 0.1 | 2.0 | 480 | 8.6 |
| 4 | 5% Pd/C | 300 | 0.1 | 1.5 | 360 | 6.4 |

* Values of amount of H₂ adsorption during 4 hrs hydrogenation are calculated from the rate data and reaction time, 4 hrs.

**Estimated values of hydrogenation conversion ratio after 4 hrs are calculated from the amount of H₂ adsorption after 4 hrs on the assumption that the selectivity of cyclohexanone/cyclohexanol is 50%/50%.

The estimated values of conversion ratio after 4 hrs are 17.9% for 5% Pt/C, 8.6% for 5% Ru/C, and 6.4% for 5% Pd/C, respectively. The reaction times for completion would be 22.3 hrs, 46.5 hrs, and 62.5 hrs, respectively. These values show that hydrogenation catalyst activities of 5% Pt/C, 5% Ru/C and 5% Pd/C are low, and that their conversion ratio values are not advantageous.

The above-discussed data from Rylander et al is now compared to comparative data in the specification herein using four catalysts: 5% Rh/C, 5% Ru/C, 5% Pt/C and 5% Pd/C, with super critical carbon dioxide. As described in the specification herein, the catalyst 19.6~78.0 mg, and 0.02 mol of phenol were put into a stainless steel high-pressure reactor of internal volume 50 ml, a pressure of 3~10 MPa of hydrogen and a pressure of 10 MPa of carbon

Application No. 10/553,792
 Reply to Office Action of November 2, 2006

dioxide were introduced in, and the hydrogenation was carried out for 10~120 min. at a reaction temperature of 55~80°C. After reaction had been completed, the hydrogen and carbon dioxide were released and the products obtained were recovered by methanol extraction, and then analyzed using a gas chromatograph. Data from thirteen examples, which are inclusive of Examples and Comparative Examples, are shown in Table A below:

Table A. Effect of four catalysts, 5% Pt/C, 5% Pd/C, 5% Ru/C and 5% Rh/C on the hydrogenation of a phenol in the carbon dioxide supercritical fluid. Experimental data were cited from the present application except the values of estimated conversion ratio.

| No. | Catalyst | | Phenol | Pressure MPa | | Temp. °C | Time min. | Conversion ratio % | Yield Selectivity % | | *Estimated conversion ratio % |
|-----|----------|-----------|--------|--------------|----------------|----------|-----------|--------------------|---------------------|-----|-------------------------------|
| | Name | Amount mg | | Mol | H ₂ | | | | none | nol | |
| CE4 | 5% Pt/C | 20.4 | 0.02 | 3.1 | 10 | 80 | 10 | 1 | 72 | 28 | 0.8 |
| CE3 | 5% Pd/C | 19.6 | 0.02 | 3 | 10.1 | 80 | 10 | 1 | 91 | 9 | 0.3 |
| E15 | 5% Ru/C | 20.6 | 0.02 | 3 | 10.1 | 80 | 10 | 11 | 69 | 31 | 0.4 |
| E14 | 5% Rh/C | 20.3 | 0.02 | 3 | 10.1 | 80 | 10 | 35 | 68 | 32 | - |
| CE2 | 5% Pt/C | 78.0 | 0.02 | 10 | 10 | 80 | 120 | 1 | 97 | 3 | 9.9 |
| CE1 | 5% Pd/C | 46.7 | 0.02 | 10 | 10 | 55 | 120 | 1 | 54 | 46 | 3.2 |
| E9 | 5% Ru/C | 63.9 | 0.02 | 10 | 10 | 55 | 120 | 30 | 5 | 95 | 4.3 |
| E4 | 5% Rh/C | 22.8 | 0.02 | 10 | 10 | 55 | 120 | 53 | 17 | 83 | - |
| E1 | 5% Rh/C | 22.8 | 0.02 | 10 | 10 | 80 | 120 | 100 | 13 | 87 | - |
| E2 | 5% Rh/C | 74.9 | 0.02 | 10 | 10 | 80 | 120 | 100 | 1 | 99 | - |
| E29 | 5% Rh/C | 20.6 | 0.02 | 9 | 10.3 | 80 | 60 | 100 | 22 | 78 | - |
| E28 | 5% Rh/C | 20.9 | 0.02 | 9 | 10.1 | 80 | 30 | 99 | 55 | 45 | - |
| E22 | 5% Rh/C | 20.8 | 0.02 | 9 | 10.4 | 80 | 10 | 70 | 50 | 41 | - |

E: Example, CE: Comparative example, none: Cyclohexanone, nol: Cyclohexanol.

Experimental data were cited from the present application except the values of estimated conversion ratio.

* Values of estimated hydrogenation conversion ratio were calculated from the H₂ adsorption rate in Modified Table V above, and reaction time in Table A on the assumption that the yield selectivity of cyclobexanone/cyclohexanol is 50%/50%.

Values of estimated hydrogenation conversion ratio were calculated from the H₂ adsorption rate in above Modified Table V and reaction time in Table A on the assumption that the yield selectivity of cyclohexanone/cyclohexanol is 50%/50%. This means that the same catalytic activities of 5% Pt/C, 5% Ru/C and 5% Pd/C in Table V of Rylander et al would be revealed under the respective carbon dioxide supercritical fluid condition. The values of H₂ adsorption rate for 0.1 mol phenol in Table 2 is revised for 0.02 mol phenol.

In the case of 5% Pt/C and 5% Pd/C, values of estimated hydrogenation conversion ratio increase with the increase of reaction time from 10 min. to 120 min.; however, experimental values of conversion ratio hydrogenated under the carbon dioxide supercritical fluid condition do not increase and indicate a constant value of 1% with the increase of reaction time from 10 min. to 120 min., although both amount of catalyst increase drastically. Therefore, catalyst activities of a phenol hydrogenation on the 5% Pt/C and 5% Pd/C using the carbon dioxide supercritical fluid are extremely weak.

On the other hand, in the case of 5% Ru/C, the value of conversion ratio hydrogenated under the carbon dioxide supercritical fluid condition increases from 11% to 30% with the increase of reaction time from 10 min. to 120 min. and the value of conversion ratio after 10 min. is 11%, and indicate 27.5 times as large compared with the value of estimated hydrogenation conversion ratio. Therefore, the phenol hydrogenation activities on the respective platinum group metal catalysts like 5% Pt/C, 5% Pd/C and 5% Ru/C under the carbon dioxide supercritical fluid condition, as in the present invention, cannot be predicted from those in water, as in Rylander et al, even if the same respective platinum group metal catalyst is used.

In the case of 5% Rh/C, experimental values of conversion ratio increase from 35% to 53% with the increase of reaction time from 10 min. to 120 min., although the reaction temperature decreases from 80°C to 55°C. Moreover, the real values of conversion ratio

Application No. 10/553,792
Reply to Office Action of November 2, 2006

drastically increase from 35% to 100% with the increase of reaction time from 10 min. to 120 min. and with the increase of amount of catalyst from 20.3 mg to 74.9 mg.

For all the above reasons, it is respectfully requested that this rejection be withdrawn.

In sum, no *prima facie* case of obviousness has been made out but even if such a case had been made out, the prior art could not have predicted the selective and superior effect that carbon dioxide has on particular platinum group metal catalysts, as recited in the present claims.

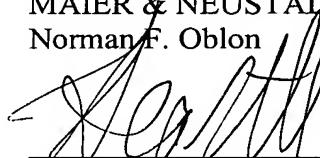
The objection to Claims 4-11, 13 and 14 as being improper multiply dependent claims is now moot in view of the above-discussed amendment. Accordingly, it is respectfully requested that the objection be withdrawn.

All of the presently-pending claims in this application are now believed to be in immediate condition for allowance. Accordingly, the Examiner is respectfully requested to pass this application to issue.

Respectfully submitted,

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